Systematic Syntheses of Heterobimetallic Complexes of Platinum with Rhodium(I), Iridium(I), Iridium(III), or Tungsten(0) bridged by Ph₂PCH₂PPh₂

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Complexes of type *trans*-[Pt(C=CR)₂(η^1 -Ph₂PCH₂PPh₂)₂] (R = Me, Ph, or *p*-tolyl), are used to effect systematic, high-yield syntheses of heterobimetallic complexes with Rh^I, Ir^I, Ir^{III} (bridging hydride), and W^o.

 $Ph_2PCH_2PPh_2$ is an excellent ligand for stabilizing homobimetallic compounds with metal-metal bonds,¹ 'A-frames,'² and 8-membered rings.^{3,4} Hitherto very few such complexes with two different metals ('heterobimetallic' complexes) have been made and methods which give homobimetallic complexes will not normally be adaptable for the synthesis of heterobimetallic complexes.

We have described high-yield syntheses of η^{1} -dppm (Ph₂PCH₂PPh₂) complexes, *trans*-[Pt(C=CR)₂(η^{1} -dppm)₂], with R = Me, Ph, or *p*-tolyl.⁵ We now show that these η^{1} -dppm complexes can be used in high-yield syntheses of hetero-

bimetallic complexes with d^8 - or d^6 -metals, viz. Rh^T, Ir^T, Ir^{TII}, and W⁰.

Treatment of *trans*-[Pt(C=CR)₂(η^1 -dppm)₂] (R = Me, Ph, or *p*-tolyl) with [Rh₂Cl₂(CO)₄] in benzene at *ca*. 50 °C for 15 min gave the orange salts [Pt(C=CR)₂(μ -dppm)₂Rh(CO)]⁺Cl⁻ in >90% yield. We formulate these complexes as (1) (X = Cl) on the basis of (i) microanalytical data; (ii) the conductivity in acetone of the Cl or PF₆ salts (1) (X = Cl or PF₆), corresponding to 1:1 electrolytes; (iii) the second-order ³¹P-{¹H} n.m.r. spectrum, shown in Figure 1; (iv) the ¹H and ¹H-{³¹P} n.m.r. spectra which show fluxionality at 20 °C, *i.e.* a broad CH₂

resonance, but at -21 °C the CH₂ resonance shows inequivalent hydrogens, one showing large coupling to ¹⁹⁵Pt, ³J(PtH) 76 Hz, and the other not showing detectable coupling; (v) the ¹⁹⁵Pt-{¹H} n.m.r. pattern (R = p-tolyl) which shows a well defined 1:2:1 triplet of doublets corresponding to ¹J(PtP) 2405 Hz, J(PtRh) 65 Hz, and ³J(PtP) ca. 0 Hz; (vi) the i.r. spectrum [e.g. for R = p-tolyl, v(C=0) 1978 cm⁻¹ and v(C=C) 2118 and 2060 cm⁻¹ (KBr disc)]. We suggest the presence of a donor-acceptor rhodium-platinum bond in these complexes



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(1) by analogy with $[Me_2Pt(\mu-dppm)_2PtMe]^+$, ^e also d⁸-d⁸; the observation of ¹⁰³Rh-¹⁹⁵Pt coupling agrees with this formulation. We also suggest that the single hydrogen of the CH₂ that is coupled to platinum in a Pt-PPh₂-C-H moiety is pseudo-equatorial as depicted in (2). The Pt-PPh₂-C-H_e dihedral (torsion) angle of 180° might be expected to give a much larger vicinal coupling, ³J(PtH_e), than the corresponding coupling to the axial hydrogen, by analogy with the well known Karplus relationship for H-C-C-H couplings.⁷ The phenomenon should be useful in assigning stereochemistry (conformation) of binuclear platinum complexes of Ph₂PCHRPPh₂ etc. (R = substituent).

When heated in boiling toluene for 3 h the salt (1) (X = Cl, R = p-tolyl) lost CO and was converted into a single, deep red, complex which we formulate as (3) (R = p-tolyl). Complex (3) was stable in boiling toluene for 10 h [³¹P- {¹H} h n.m.r. evidence]. When treated with carbon monoxide in toluene at 20 °C (3) (R = p-tolyl) rapidly gave the orange salt (1) (X = Cl) in essentially quantitative yield. Treatment of $[Rh_2Cl_2-(C_8H_{14})_4](C_8H_{14} = cyclo-octene)$ with $[Pt(C=C-p-tolyl)_2(\eta^1-dppm)_2]$ also gave (3).

Treatment of *trans*-[IrCl(CO)(PPh₃)₂] with [Pt(C=C-*p*-tolyl)₂(η^1 -dppm)₂] in refluxing benzene gave, after 5 min, a deep purple solution which paled to red after 1 h. From the solution the yellow neutral complex, [Pt(C=C-*p*-tolyl)₂-(μ -dppm)₂IrCl(CO)] (4) was isolated in >80% yield. The formulation follows from microanalytical, i.r., and n.m.r. data as for the rhodium complexes (above). We have not identified the purple intermediate. Treatment of [Ir₂Cl₂(C₈H₁₄)₄] with [Pt(C=CPh)₂(η^1 -dppm)₂] (1:1 proportion) in C₆H₆ at 20 °C gave the dark green neutral complex [(PhC=C)₂Pt(μ -dppm)₂-IrCl] (5) (fully characterized). This reacted rapidly with H₂ (1 atm) to give a yellow dihydride [(PhC=C)₂Pt(μ -dppm)₂-(μ -H)IrHCl] (6). This structure is based on elemental analysis (C, H, Cl), the i.r. and ³¹P-{¹H} n.m.r. spectra, and particu-



Figure 1. ³¹P-{¹H} N.m.r. spectrum (161 MHz) of $[Pt(C=C-p-tolyl)_2(\mu-dppm)_2Rh(CO)]Cl in CDCl₃ at 20 °C. <math>\delta(P_A)$ (platinum) 1.2 p.p.m., ¹J(PtP_A) 2357 Hz, $\delta(P_B)$ (rhodium) 20.2 p.p.m., ¹J(RhP_B) 112 Hz, $J(P_AP_B) + J(P_AP_B)$ 43 Hz.



larly the ¹H and ¹H-{³¹P} n.m.r. spectra. The ¹H-{³¹P} n.m.r. spectrum in the hydride region showed a resonance at δ -12.5 p.p.m. as a broad doublet, ²J(HH) *ca.* 2 Hz with satellites due to platinum-195, ¹J(PtH) 615 Hz. We assign this to the bridging hydrogen shown in (6). Similar values for ¹J(PtH) are also found for a bridging hydrogen in [Pt₂H₃(μ -dppm)₂]⁺⁸ or [Et₃P(Ph)Pt(μ -H)₂IrH(PEt₃)₂]^{+.9} The resonance of the second hydride in (6) occurs at δ -19.85 p.p.m. ²J(HH) *ca.* 2 Hz, ³J(PtH) 25 Hz.

Treatment of *trans*-[Pt(C=CR)₂(η^1 -dppm)₂] with *fac*-[W-(CO)₃(NCMe)₃] in refluxing benzene for 2 h gave a single, dark red, binuclear platinum-tungsten complex in each case: we tentatively formulate these as (7) (R = Me, Ph, or *p*-tolyl). Yields were *ca.* 40%. This formulation is based on elemental analysis, i.r., and ³¹P-{¹H}, ¹H-{³¹P}, and ¹⁹⁵Pt{¹H} n.m.r. spectroscopy.

We believe that it will be possible to carry out much chemistry with the above-mentioned complexes without breaking down the heterobimetallic system. Thus preliminary ³¹P-{¹H}, ¹H, and ¹H-{³¹P} n.m.r. studies show that [(PhC=C)₂-Pt(μ -dppm)₂IrCl(CO)] reacts rapidly with NaBP₄, NaBF₄, or NH₄PF₆ to give a single cationic species, presumably the iridium analogue of (1), which in turn reacts with H₂ (to give a dihydride), CO, allene, buta-1,3-diene, PhC=CH, *etc.* to give a *single* heterobimetallic product (different in each case). Rhodium-platinum complexes of type (1) react immediately with NaBH₄ or LiBEt₃H to give an intensely red product.¹⁰

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